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**14. ABSTRACT**

Direct absorption IR laser methods developed under AFOSR support have been used to study state-to-state reactive scattering dynamics in collisions systems under crossed supersonic jet, single collision conditions. This past year has focused on reaction dynamics in three collision systems, i) $F + HD \rightarrow HF(v,J) + D$, ii) $F + CH_4 \rightarrow HF(v,J) + CH_3$, iii) $F + NH_3 \rightarrow HF(v,J) + NH_2$. Time resolved flash kinetic studies of the $OH/HO_2/O_3$ chemical chain reaction has been performed from 300K down to 190K, providing first access to temperature conditions relevant to accurate modeling of the lower stratosphere. Most recently, these methods have been extended to study "airglow" dynamics of highly rotationally excited OH(v,N) radicals formed from $H+O_3$ reactions.

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**AFOSR/AASERT Final Report: 9/1/00**
**State-to-state thermal/hyperthermal collision dynamics of atmospheric species**

**Abstract:**

Direct absorption IR laser methods developed under AFOSR support have been used to study state-to-state reactive scattering dynamics in collisions systems under crossed supersonic jet, single collision conditions. This past year has focused on reaction dynamics in three collision systems, i) F + HD $\rightarrow$ HF(v,J) + D, ii) F + $CH_4$ $\rightarrow$ HF(v,J) + $CH_3$, iii) F + $NH_3$ $\rightarrow$ HF(v,J) + $NH_2$. Time resolved flash kinetic studies of the $OH/HO_2/O_3$ chemical chain reaction has been performed from 300K down to 190K, providing first access to temperature conditions relevant to accurate modeling of the lower stratosphere. Most recently, these methods have been extended to study "airglow" dynamics of highly rotationally excited OH(v,N) radicals formed from H+$O_3$ reactions.

**Brief overview of work:**

Direct absorption IR laser methods developed under AFOSR support have been used to study state-to-state reactive scattering dynamics in collisions systems under crossed supersonic jet, single collision conditions. This past year has focused on reaction dynamics in three collision systems, i) F + HD $\rightarrow$ HF(v,J) + D, ii) F + $CH_4$ $\rightarrow$ HF(v,J) + $CH_3$, iii) F + $NH_3$ $\rightarrow$ HF(v,J) + $NH_2$, corresponding to our proposed plan to move from atom + diatom systems onto more complicated atom + polyatom reactive scattering.

In the F + HD system, the key interest is in the probing of long lived "quantum scattering resonances" at the transition state. This resonances correspond to well developed vibrational nodal structure in wave packet calculations, and recently predicted by Skodje et al to occur at $E_{com} \approx 0.5$ kcal/mole. Theory predicts a dramatic shift in nascent state populations in the HF(v=2,J) manifold in the scattering resonance regime, essentially from a more smooth Boltzmann-like J distribution to a relatively "flat-top" albeit structured distribution which drops off rapidly at the energetic limit. The results are shown in Fig. 1, which are in remarkably good agreement with wave packet theoretical calculations. This is particularly interesting in light of the immense effort that has been invested in attempts to verify similar resonance scattering behavior in the F + $H_2$ system, where in fact it appears that all resonance structure in $FH_2^-$ photodetachment can now be theoretically assigned to van der Waals angular momentum barriers.

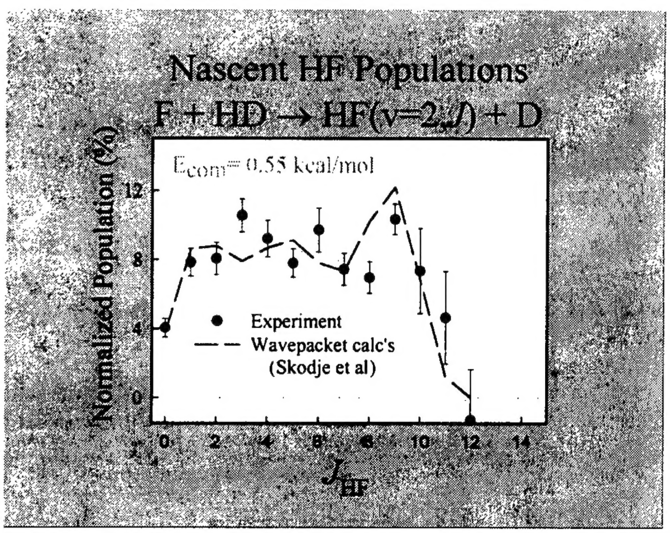


Fig 1. F+HD reactive scattering into HF(v=2,J) manifold near the transition state resonance predicted at 0.5 kcal.mole: experiment vs theory

In a second direction, efforts toward atom + polyatom reactive scattering have been pursued. State-to-state reactive scattering of F + $CH_4$ $\rightarrow$ HF(v,*J*) + $CH_3$ is studied using crossed supersonic jets and high-resolution ($\Delta\nu \approx 0.0001$ cm$^{-1}$) IR laser direct absorption

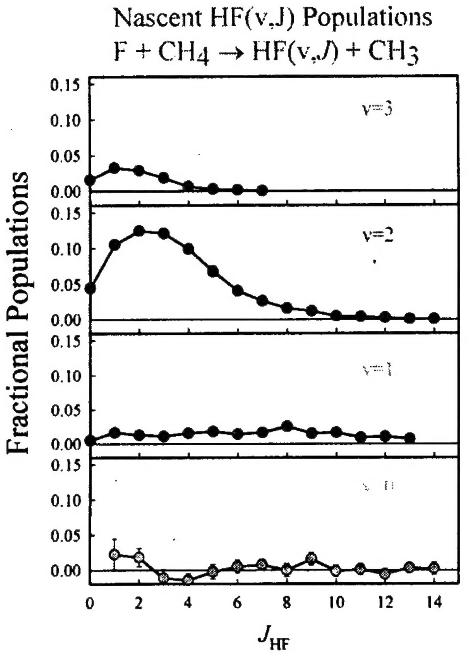


Fig 2. Nascent populations from F + $CH_4$ reactive scattering

techniques. Rovibrational state-resolved HF column-integrated absorption profiles are obtained under single collision conditions and converted to populations via appropriate density-to-flux transformation. Nascent rovibrational distributions in each HF(v,*J*) state are now available (Fig. 2) and reported in the literature. Summed over all product rotational levels, the nascent *vibrational* quantum state populations for HF(v) [v=3: 0.106(3); v=2: 0.667(14); v=1: 0.189(27); v=0: 0.038(78); $2\sigma$ error bars] are in agreement with previous flow cell studies by Setser, Heydtmann, and co-workers [Chem. Phys. **94**, 109 (1985)]. At the *rotational* state level, however, the current studies indicate nascent distributions for HF(v,*J*) that are significantly hotter than previously reported, ostensibly due to reduced collisional relaxation effects under supersonic jet conditions. Final HF rotational states from F + $CH_4$ are observed near the maximum energetically accessible *J* values in both the v=2 and v=3 vibrational manifolds, which provides experimental support for a bent F-H-C transition state structure.

In addition, product recoil data from F + $CH_4 \rightarrow$ HF(v,*J*) + $CH_3$ reactive scattering are obtained using crossed supersonic jets and narrow band ($\Delta\nu \approx 0.0001$ cm$^{-1}$) IR laser direct absorption techniques. The high resolution IR profiles of HF(v,J) product exhibit extensive Doppler broadening that directly reflects quantum state-resolved *translational* distributions in the laboratory frame under collision free conditions. Analysis of Doppler profiles via singular value decomposition (SVD) methods yield information on state-resolved differential cross sections into the HF (v=1) and HF(v=2) vibrational manifolds, which identify a small propensity for forward/backward scattering ($|\cos(\theta)| \approx 1$) vs. side scattering ($|\cos(\theta)| \approx 0$) in the center of mass frame. This can be nicely seen in terms of a plot of experimentally observed recoil kinetic energy along the IR probe (z) direction vs total available energy (Fig 3). When compared with the theoretical predictions for purely sideways or isotropic scattering, the data clearly indicates a systematic shift toward more forward/backward than isotropic behavior.

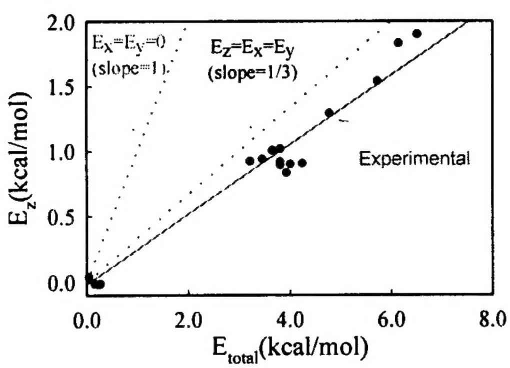


Fig 3. HF(v,J) z axis recoil translational energy from F+$CH_4$ reactive events, indicating small propensity for forward/backward scattering

We have most recently been studying the F + $NH_3$ system, which has now yielded first rigorously collision free HF(v,J) populations for this reaction. There is a interesting bimodality in the HF(v=1,2) rotational distributions, specifically a long tail toward higher J levels that may indicate two different channels in the reaction mechanism.

Time resolved flash kinetic studies of the $OH/HO_2/O_3$ chemical chain reaction has been performed from 300K down to 190K, providing first access to temperature conditions relevant to accurate modeling of the lower stratosphere (Fig. 4). Most recently, these methods have been extended to study "airglow" dynamics of highly rotationally excited OH(v,N) radicals formed from $H+O_3$ reactions. Preliminary work has indicated the presence of high rotational levels up to N ≈ 33, as indeed directly observed in the upper atmosphere by efforts in the Air Force laboratories. Further work in progress will be necessary to distinguish between direct formation into high N states versus anomalously rapid and efficient V-R transfer from the highest vibrational manifold.

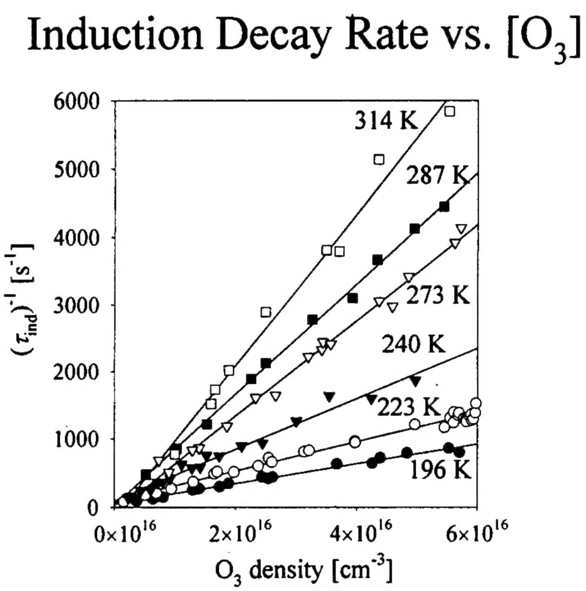


Fig 4. Temperature dependent rate constant data for $OH/HO_2/O_3$ chemical chain reaction kinetics

**Awards or Fellowships received 1999-2000**

William F. Meggers Award, Optical Society of America 1999

Alexander von Humboldt Fellowship, Humboldt Foundation, 1999-2000

**Graduate students supported by AASERT grant:**

Scott Davis

William Chapman

Bradley Blackmon

Joanna Fair

Evan Jochnowitz

**Papers published, in press or submitted since last progress report acknowledging AFOSR support:**

1) S. A. Nizkorodov, W. W. Harper and D. J. Nesbitt, "State-to-state reaction dynamics in crossed supersonic jets: threshold evidence for non-adiabatic channels in $F + H_2$", Faraday Disc. 113, 107 (1999).

2) J. R. Fair and D. J. Nesbitt, "Dynamics of Collisional Alignment in Supersonic Expansions: Trajectory Studies of He + CO, $O_2$ and $CO_2$", J. Chem. Phys. 111, 6821 (1999).

3) S. A. Nizkorodov, W. W. Harper, W. B. Chapman, B. W. Blackmon and D. J. Nesbitt, "Energy dependent cross sections and non-adiabatic reaction dynamics in $F(^2P_{3/2}, ^2P_{1/2})$ + n-$H_2 \rightarrow$ HF(v,J) + H", J. Chem. Phys. 111, 8404 (1999).

4) S. Davis, D. Uy, and D. J. Nesbitt, Laser spectroscopy of jet-cooled ethyl radical: Infrared studies in the $CH_2$ stretch manifold", J. Chem. Phys. 112, 1823 (2000).

5) S. A. Nizkorodov, W. W. Harper, B. W. Blackmon and D. J. Nesbitt, "Temperature dependent kinetic studies of the $OH/HO_2/O_3$ chain reaction by time resolved high resolution laser absorption spectroscopy", J. Phys. Chem 104, 3964 (2000).

6) W. W. Harper, S. A. Nizkorodov, and D. J. Nesbitt, "Quantum state-resolved reactive scattering of $F + CH_4 \rightarrow$ HF(v,J) + $CH_3$: Nascent HF(v,J) product state distributions", J. Chem. Phys. (in press).

**Invited talks since last progress report acknowledging AFOSR support:**

"Non-adiabatic reaction dynamics in F + n-$H_2$ from IR laser based state-to-state reactive scattering studies", American Chemical Society ($218^{th}$ National Meeting), New Orleans, LA, August 23, 1999.

"Single particle microscopy above and below the diffraction limit", Optical Society of America, Santa Clara, CA, September 28, 1999.

"Chemical physics with lasers: From slit jet discharges to single molecule spectroscopy", Department of Chemistry, University of Wisconsin, Madison, WI, October 26, 1999.

"Where Chemistry meets Physics", CU Wizards Science Outreach Program, Department of Chemistry, University Colorado, Boulder, CO, October 30, 1999.

"From state-to-state reaction dynamics to single molecule microscopy", Department of Chemistry, University of Maryland, College Park, MD, November 11, 1999.

"Chemical dynamics with a twist: From state-resolved reactions in supersonic jets to single molecule microscopy", Department of Chemistry, University of Southern California, Los Angeles, CA, January 10, 2000.

“Chemical kinetics with a twist: From state-to-state reaction dynamics to single molecule microscopy”, Department of Chemistry, University of Arizona, Tucson, AZ, January 24, 2000.

“Microscopy at and below the diffraction limit via resonant scattering and laser induced fluorescence: Recent progress from apertureless NSOM”, American Physical Society, Minneapolis, MN, March 21, 2000.

“Probing quantum state to state dynamics: From clusters to chemical reactions”, American Chemical Society (219$^{th}$ national Meeting), San Francisco, CA, March 26, 2000.

“From Single Collisions to Single Molecules”, Institute for Physical Chemistry, University of Goettingen, Goettingen, Germany, April 13, 2000

“Spectroscopy above and below the diffraction limit”, Max Planck Institute for Biophysical Chemistry, Goettingen, Germany, April 28, 2000.

“State-resolved IR Laser Studies of Fundamental Reaction Dynamics”, Atomic and Molecular Interactions Gordon Conference, New London, NH, July 4, 2000.

“Spectroscopy, kinetics and single collision dynamics via high resolution IR laser studies of radicals”, 16th International Symposium on Gas Kinetics, Cambridge, UK, July 23, 2000.